

## 'Roll-over' 3-Metallation of Co-ordinated 2,2'-Bipyridyl in the Thermal Rearrangement of Diaryl(bipyridyl)platinum(II) Complexes: Molecular Structure of $(\mu\text{-bidyl})[\text{PtPh}(\text{Bu}^t\text{py})]_2^\dagger$

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Thermal rearrangement of diaryl(2,2'-bipyridyl)platinum(II) complexes normally proceeds *via* consecutive 3-metallations of the bipyridyl ligand with hydrogen migration and elimination of two equivalents of arene, while, in the presence of free pyridine, the process can be interrupted at a monoarylplatinum intermediate by formation of a dinuclear pyridine adduct whose molecular structure has been determined.

Intramolecular hydrogen migrations are some of the most commonly encountered routes controlling the reactivity of organotransition metals.  $\beta$ -Hydrogen transfer from hydrocarbyl ligands generally takes place most readily,<sup>1</sup> but where this is suppressed, more remote C-H activations occur instead, including a great array of C-metallations on various ancillary ligands.<sup>2,3</sup> Recognising the capacity of the 2,2'-bipyridyl ligand to act as a hydrogen transfer source *via* 'roll-over' 3-metallation<sup>4</sup> we have begun exploration of the reactivity of its organoplatinum complexes. Although a few examples of metallation on 2,2'-bipyridyl have appeared recently,<sup>5</sup> it has not previously featured as a labilising route for organometallic molecules  $(\text{bipy})\text{MR}_n$ . Here we present preliminary results of our studies. Complexes (**1a**–**c**) eliminated 1.7–1.9 equivalents of Ar-H upon heating in toluene solutions. Coupling of aryl groups was not significant (~0.5 mole%) in sharp contrast to the behaviour of diorganonickel analogues<sup>6</sup> and of diarylplatinum complexes with monodentate phosphine ligands.<sup>7</sup> When reaction was carried out in  $[\text{D}_8\text{H}_8]$ toluene, no incorporation of deuterium into arene products was observed. Concomitant with arene elimination in each case was precipitation of an orange-brown compound (**5**), whose insolubility precluded recrystallisation, but whose elemental analyses indicated an empirical formula approximately  $\text{C}_{10}\text{H}_8\text{N}_2\text{Pt}$ . I.r. spectroscopy confirmed the presence of a co-ordinated bipyridyl while, in the products from (**1b**) and (**1c**), absorptions due to the t-butyl and trifluoromethyl functions had largely disappeared. When a suspension of the solid in dimethyl sulphoxide was treated with dry HCl,  $(\text{bipy})\text{PtCl}_2$  was the predominant inorganic product identified.

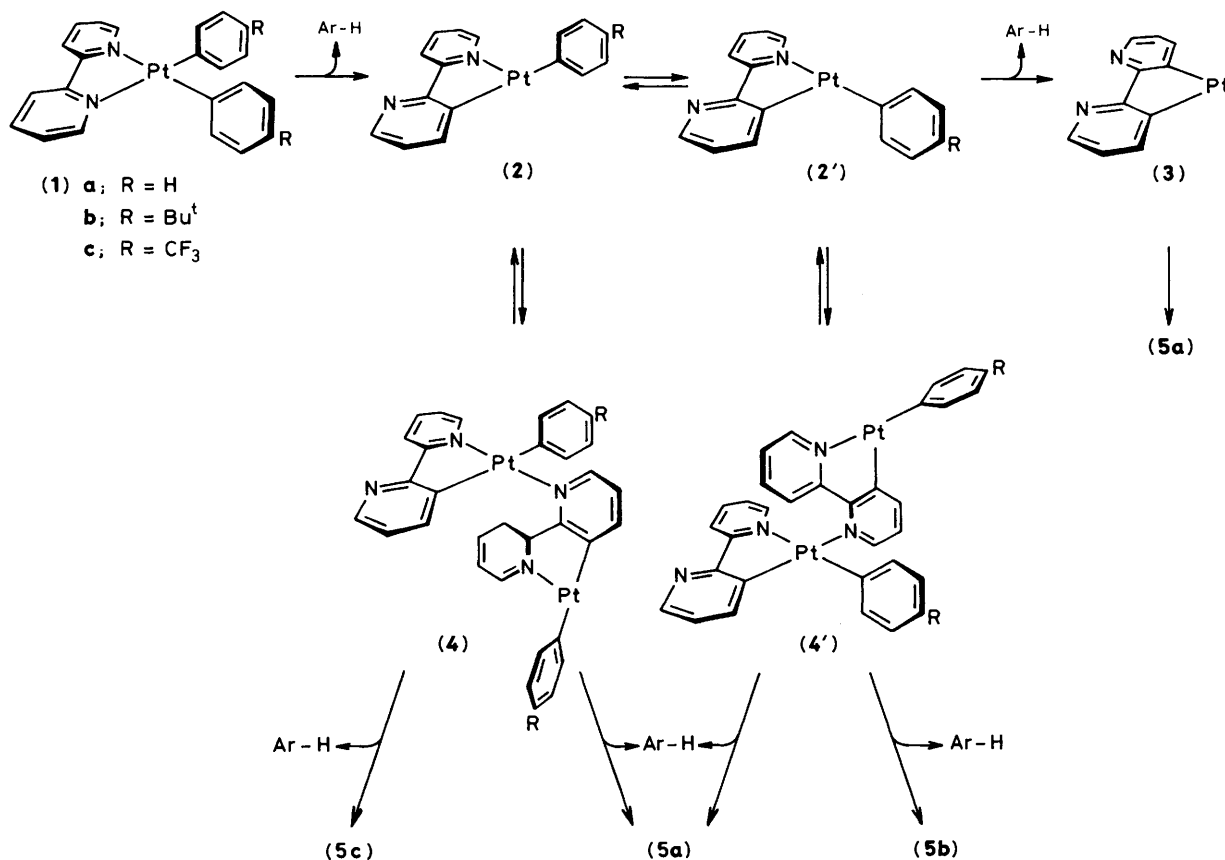
The extent of arene evolution, and the non-incorporation of deuterium, effectively exclude both  $\beta$ -hydrogen migration

from an aryl ligand,<sup>8</sup> and hydrogen abstraction from solvent, either *via* direct attack by  $(\text{bipy})\text{PtAr}_2$ , or by aryl radicals following Pt-C homolysis, as sources of the transferred hydrogen. The absence of biaryls<sup>9</sup> and of solvent-derived products such as bibenzyl and diarylmethanes is further disproof of radical pathways, in contrast with reported reactivity of dialkyl(2,2'-bipyridyl)platinum(II).<sup>10</sup> These data suggest that the major rearrangement route for these systems involves hydrogen transfers from bipyridyl to aryl ligands, most plausibly *via* 3-metallation. The primary organometallic product of these processes would be expected to be polymeric, of isomeric forms (**5a**), (**5b**), or (**5c**).

The very poor solubility of (**1a**) rendered it unsuitable for precise kinetic measurements, but the reactions of (**1b**) and (**1c**) were monitored by h.p.l.c. and  $^1\text{H}$  n.m.r. spectroscopy. In both cases decay of  $(\text{bipy})\text{PtAr}_2$  was first order in parent complex [for (**1b**),  $k$  (423 K)  $3.26 \times 10^{-4} \text{ s}^{-1}$ ; for (**1c**),  $k$  (423 K)  $5.27 \times 10^{-6} \text{ s}^{-1}$ ]. The overall appearance of arene, however, conformed to neither a first- nor a second-order rate law. These observations accord with a scheme in which the step responsible for loss of (**1**) is unimolecular, generating a single arene, whereas the production of the second arene has more complex molecularity. Scheme 1 summarises such a mechanism. An intramolecular 'roll-over' 3-metallation generates (**2**) from (**1**), releasing arene. A quasi T-shaped geometry is most likely for (**2**), but configurational lability is also highly probable,<sup>11,12</sup> and a *cisoid* arrangement of Pt-C bonds (**2'**) would be more thermodynamically favourable.

A second roll-over metallation, affording the energetically improbable 12-electron species (**3**), is unlikely at this stage. More plausible and kinetically consistent is that (**2**) co-ordinates with other molecules of itself (or isomer) *via* the freed nitrogen, yielding, for example, dinuclear species (**4**) and/or (**4'**). Arene elimination can now be accomplished

$\dagger$  bidyl = 2,2'-bipyridyl-3,3'-diyl; Bu<sup>t</sup>py = 4-t-butylpyridine.



either by a second roll-over metallation or else by 3-metallation on the newly co-ordinated fragment without preliminary Pt-N scission. In either case, successive combination-metallation steps will result in oligomerisation which will eventually lead to precipitation of the polymeric (5). We are unable to deduce the isomeric nature of (5), and, therefore, the relative roles of (4) and (4') [or (3)], nor, indeed, can we be certain of the nuclearity of (4) prior to metallation-arene elimination.‡

In an effort to intercept co-ordinatively unsaturated intermediates such as (2) or to trap (4) [or (3)] prior to further polymerisation, we investigated the effect of pyridine and 4-*t*-butylpyridine ( $\geq 10$  equiv.) on the thermolyses of (1a) and (1b). Here, one equivalent of arene as well as half an equivalent of bipyridyl were the only soluble products. In each case, an orange crystalline compound was produced, whose i.r. characteristics and elemental analyses suggested dinuclear species (6). Their insolubility precluded n.m.r. discrimination between the several possible isomers, and so the product (6) of reaction of (bipy)PtPh<sub>2</sub> in presence of *t*-butylpyridine was

‡ The growing polymer should always contain at least one metal-bound aryl and an unmetallated bipyridyl ring, and if polymer insolubility is the major control on the extent of oligomerisation, then some arylmetal functionality should be lost from solution prior to M-C scission. During rearrangement of (1b), <sup>1</sup>H n.m.r. spectra showed a gradual decrease in the total signal due to all *t*-butyl substituents of soluble species, which is also consistent with the general production of <2 equiv. of arene upon complete thermolysis of (1). Residual (5), moreover, retains some i.r. characteristics of aryl substituents, and liberates arene (5–10 mole%) when treated with HCl in Me<sub>2</sub>SO.

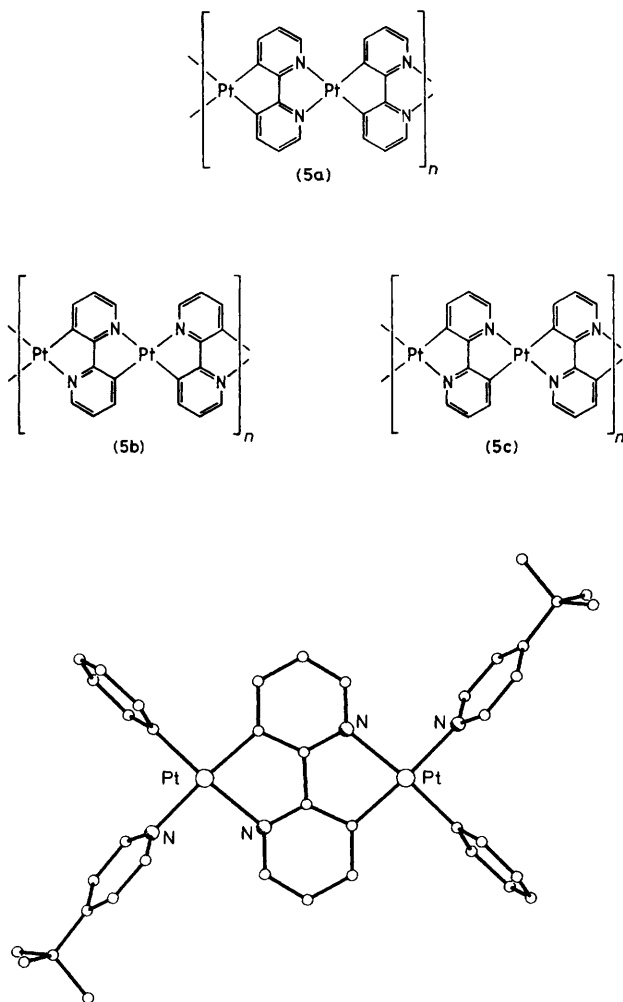
examined by X-ray diffraction, and was proved to have *cis*-arrangements of ligating nitrogen atoms on each platinum atom.

*Crystal data:* C<sub>40</sub>H<sub>42</sub>N<sub>4</sub>Pt<sub>2</sub>, triclinic, space group  $P\bar{1}$ ,  $a = 8.984(1)$ ,  $b = 10.502(2)$ ,  $c = 19.593(3)$  Å,  $\alpha = 80.82(1)$ ,  $\beta = 87.59(1)$ ,  $\gamma = 80.19(1)^\circ$ ,  $U = 1798.0$  Å<sup>3</sup> (at 20 °C),  $Z = 2$ . X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an  $\omega$ -scan technique with graphite monochromated Cu-K $\alpha$  radiation. 3686 Independent reflections were measured (to  $\theta = 50^\circ$ ), of which 745 were 'unobserved.' The structure was solved by direct methods and least-squares refinement has now reached  $R = 0.034$ .§ The programme system SHELXTL<sup>13</sup> was used.

There are two crystallographically independent molecules in the structure, each of which lies on a centre of symmetry. Apart from minor differences in orientations of rings, there are no chemically significant differences between the two independent molecules. The structure of one molecule is shown in Figure 1. The identification of the metal-bonded C and N atoms in the bidyl entity is supported by (a) their temperature factors, (b) the consistent variations in Pt-N and Pt-C bond lengths, and (c) the C-N and C-C distances in the rings.

The structure supports the view that these complexes

§ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 1.** Molecular structure of  $(\mu\text{-bidyl})[\text{PtPh}(\text{Bu}'\text{py})]_2$  (**6**). Mean bond lengths: Pt–N(bidyl) 2.142(9), Pt–N(Bu'py) 2.107(7), Pt–C(bidyl) 1.996(9), Pt–C(Ph) 1.993(10) Å; the main distortion in the square-planar metal co-ordination is the N–Pt–C chelate angle of  $81.7(4)^\circ$ .

rearrange by an intramolecular metallation followed by oligomerisation *via* attack at a second metal centre. Disappearance of (**1b**) was uniformly first-order, in accord with a unimolecular step  $\{k(423\text{ K}) 4.31 \times 10^{-4} \text{ s}^{-1}; [\text{py}]/[\text{Pt}] 10:1\}$  but during the reaction at least two other *t*-butylphenyl platinum species could be detected by  $^1\text{H}$  n.m.r. spectroscopy, as well as the product  $\text{PhCMe}_3$ . Reduction in the total *t*-butyl signal intensity, however, conformed to a *second-order* rate law consistent with the bimolecular formation of (**6**) whose insolubility removes it immediately from the system.

Although the basic elements of the rearrangement remain the same, the presence of large excesses of pyridines affects its course, as (**6**) is clearly the product of reaction of (**2b**) with a non-cyclometallated species with simultaneous or prior release of 2,2'-bipyridyl. We have not yet been able to isolate mono-metallated intermediate(s), in contrast to a related cyclometallation on the tris(pyrazolyl)methane ligand.<sup>14</sup>

The corresponding reactions of the 4,4'-dimethyl-2,2'-bipyridyldiaryplatinum(II) complexes have also been studied. Their rearrangements exactly parallel those of  $(\text{bipy})_2\text{PtAr}_2$ , but are uniformly slower; for  $(\text{Me}_2\text{bipy})\text{Pt}(\text{C}_6\text{H}_4\text{Bu}^t\text{-4})_2$ ,  $k(423\text{ K}) 4.43 \times 10^{-6} \text{ s}^{-1}$ . This is presumably due to the more bulky substituent adjacent to the metallation site.

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